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VIBRATIONAL OVERTONE SPECTROSCOPY OF BENZENE AND PYRIDINE
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by

Ph. Avouris and J. E. Demuth

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Vibrational Overtone Spectroscopy of Benzene and Pyridine on Ag(111)[†]

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Vibrational overtone spectroscopy of polyatomic molecules has received considerable attention¹ due to its importance in understanding the character of higher vibrational states and its direct relevance to gas phase studies of single-photon² and multiphoton³ vibrational chemistry. Similarly overtone spectroscopy of adsorbed molecules is important in understanding vibrational photochemistry on (metal) surfaces⁴⁻⁹ and more importantly in probing changes in intramolecular bonding upon binding to the surface.^{10,11} However, such spectroscopy has not been experimentally possible because of the small cross sections for optical excitation and the low density of adsorbed species on surfaces.

In this Communication we present the first electron scattering study which allows the detection of vibrational overtones for monolayer coverages of adsorbed species. We present results on the C-H overtones of pyridine and benzene adsorbed under UHV conditions on a Ag(111) surface. We observe these optically forbidden overtones by utilizing short-range, non-dipolar, electron scattering mechanisms, i.e. impact¹² and resonance scattering via temporary negative ion states.¹³ The electron energy loss spectrometer used in these studies (with ~20meV resolution) and the details of the preparation of the Ag surface are described elsewhere.¹⁴

In Fig. 1 we show the overtone spectra of pyridine at a saturation monolayer coverage. We note that, while the lineshape of the $|0\rangle \rightarrow |2\rangle$ transition is almost symmetric, a distinct shoulder appears in the $|0\rangle \rightarrow |3\rangle$

transition, and, finally, the $|0\rangle \rightarrow |4\rangle$ transition is clearly split. The splitting of the pyridine overtones can be explained on the basis of inequivalent α and β,γ groups of C-H oscillators. On the basis of the relative integrated intensities we assign the lower frequency peak to the β,γ -CH oscillators. The spectra for benzene show only a single peak up to $|4\rangle$ and are not displayed here.

In Fig. 2 we show the fit of the overtone energies of adsorbed benzene, about half a monolayer on Ag(111), to the Birge-Sponer relationship¹: $\Delta E_v \cdot v^{-1} = A + B \cdot v$, where ΔE_v is the $|0\rangle \rightarrow |v\rangle$ transition energy, A is the local mode frequency, and B is the diagonal anharmonicity. A linear plot is obtained, giving $A=3095\text{cm}^{-1}$ and $B=-48\text{cm}^{-1}$. The corresponding values for liquid benzene¹⁵ are $A=3095\text{cm}^{-1}$ and $B=-58.4\text{cm}^{-1}$. The Birge-Sponer plot for β,γ -CH oscillators of adsorbed pyridine gives $A=3092\text{cm}^{-1}$ and $B=-51\text{cm}^{-1}$; while for liquid pyridine¹⁶, $A=3094\text{cm}^{-1}$ and $B=-56\text{cm}^{-1}$. It appears that, upon adsorption, there is a minimal change in A but B is reduced significantly. This fact implies a higher C-H dissociation energy for the adsorbed molecule.

These changes can be the result of both a change of phase and of the involvement of specific metal-molecule interactions. In this respect the liquid-to-solid phase change in 3-methylpentane has been reported to result in a 5cm^{-1} reduction in the C-H anharmonicity.¹⁷ Bond dipole-image dipole coupling could also be involved. In the case of benzene, which lies flat on the

Ag surface¹⁴, we estimate a decrease of B by $\sim 3\text{cm}^{-1}$ due to this type of coupling. The smaller reduction in B for pyridine may reflect the fact that it is bonded by the nitrogen lone pair rather than π -bonded (as benzene is) to Ag(111) under our conditions.¹⁸ More experiments are needed to verify if the observed reduction is anharmonicity is a general occurrence among physisorbed molecules.

In Fig. 2 we also show the variation of the width (corrected for instrumental broadening) of the overtone states of adsorbed benzene as a function of v (dotted line). The corresponding widths for pyridine (α and β,γ peaks) are smaller ($\sim 360\text{cm}^{-1}$ for $|4\rangle$ of the β,γ -CH mode) and do not follow a linear dependence. The observed linewidths can have contributions from lifetime broadening, librational broadening¹⁹, and inhomogeneous broadening. Because of the expected steeper librational potential in the adsorbed state (vs. the liquid) and the low surface temperature the contribution from librational broadening is expected to be minimal. Similarly, we expect minimal contribution from inhomogeneous broadening, as we have an idealized, clean and annealed single crystal surface upon which the molecules are weakly adsorbed ($\leq 10\text{kcal/mole}$). In the gas phase the homogeneous linewidth of $|4\rangle$ is calculated to be $\sim 130\text{cm}^{-1}$.²⁰ In the liquid state ($\sim 300\text{K}$) where librational broadening occurs the $|4\rangle$ linewidth of benzene is $\sim 180\text{cm}^{-1}$.²¹ The linewidth of $|4\rangle$ for benzene on Ag is significantly larger, $\sim 630\text{cm}^{-1}$. Thus a lower limit to the total relaxation time T_2 ($T_2^{-1} = (2T_1)^{-1}$) (population

relaxation) + $T_2'^{-1}$ (phase relaxation)) of $|4\rangle$ can be obtained as $T_2 = (\pi\Delta\nu)^{-1} \cong 2 \times 10^{-14}$ sec.

Several non-radiative mechanisms have already been discussed which can greatly shorten the T_1 of an excited molecule near a metal surface.^{22,24} Since overtone transitions have very small dynamic dipoles, relaxation must proceed primarily via mechanisms involving non-dipolar coupling.²⁴ In the case of the dipole-allowed ${}^1B_{2u} \leftarrow {}^1A_{1g}$ electronic transition of pyrazine on Ag(111), we have deduced^{14,25} an even shorter total relaxation time $T_2 \cong 5 \times 10^{-15}$ sec. The fast relaxation of the overtones of adsorbed molecules suggested by our data will severely limit any selective multiphoton vibrational chemistry for molecules adsorbed on metals.

We would like to thank Professor A. C. Albrecht for a useful discussion.

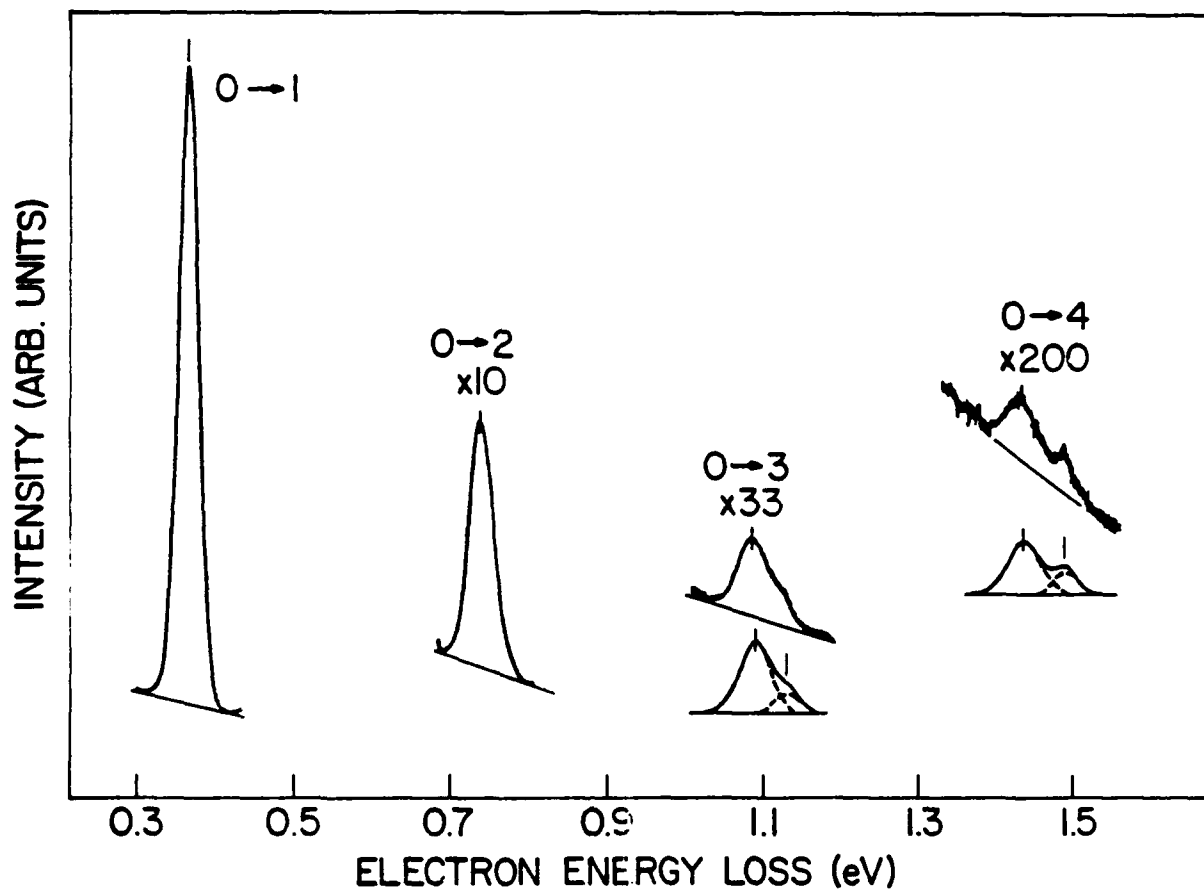
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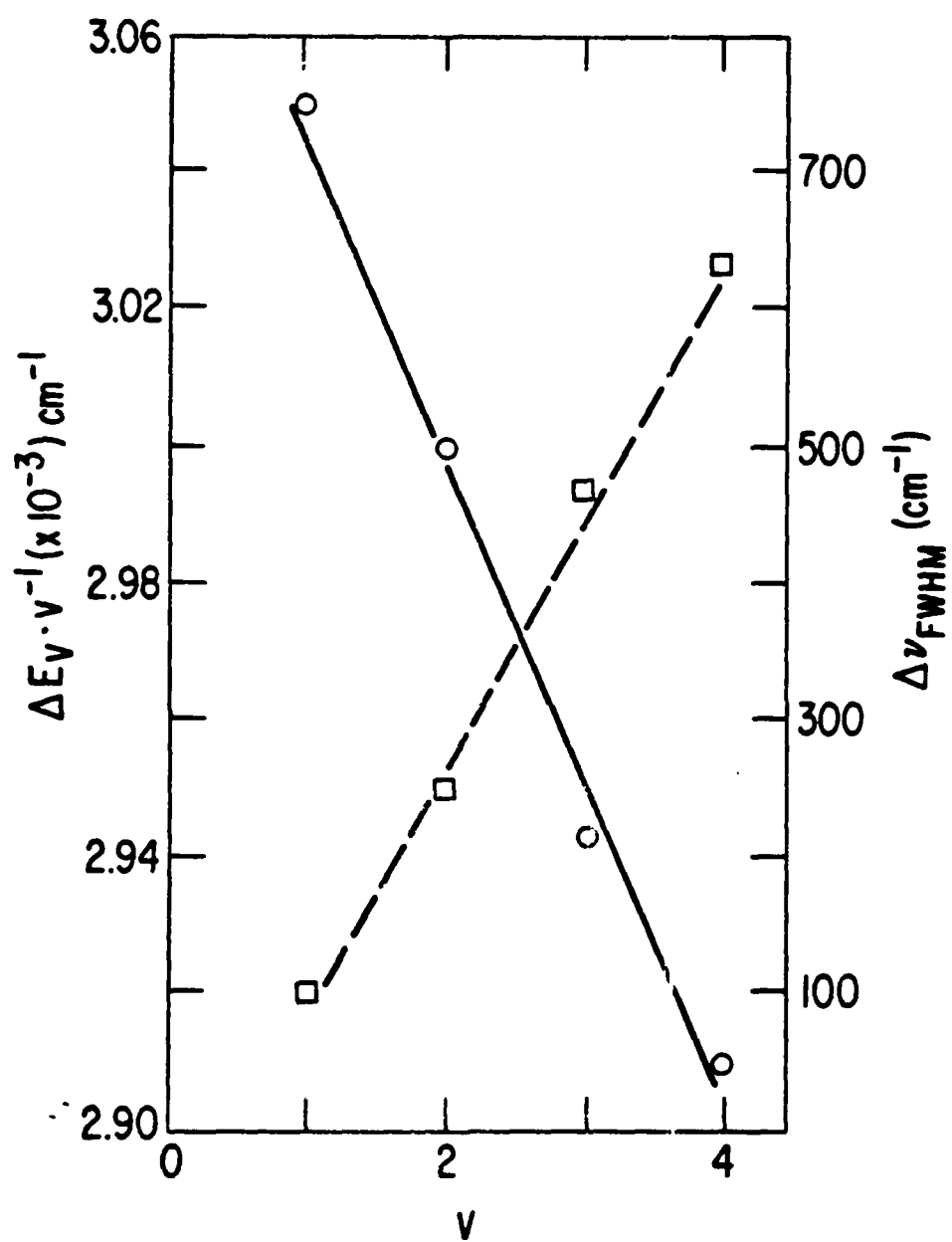
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Figure Captions

- Figure 1** Electron energy loss spectra of the C-H overtones of pyridine (1 Langmuir) on Ag(111) at 140K. Electron beam energy $E_B \sim 4\text{eV}$.
- Figure 2** Birge-Sponer plot for the C-H overtones of benzene (1 Langmuir) on Ag(111) at 140K, $E_B \sim 3.5\text{eV}$ (solid line); linewidth (full width at half maximum) of these overtones as a function of the vibrational quantum number v (dotted line).





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